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**Organic surfactants
on sea salt aerosols**

L. Smoydzin and
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Do organic surface films on sea salt aerosols influence atmospheric chemistry? – A model study

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Abstract

Organic material from the ocean's surface can be incorporated into sea salt aerosol particles often producing a surface film on the aerosol. Such an organic coating can reduce the mass transfer between the gas phase and the aerosol phase influencing sea salt chemistry in the marine atmosphere. To investigate these effects and their importance for the marine boundary layer (MBL) we used the one-dimensional numerical model MISTRA. We considered the uncertainties regarding the magnitude of uptake reduction, the concentrations of organic compounds in sea salt aerosols and the oxidation rate of the organics to analyse the possible influence of organic surfactants on gas and liquid phase chemistry with a special focus on halogen chemistry. By assuming destruction rates for the organic coating based on laboratory measurements we saw a rapid destruction of the organic monolayer within the first meters of the MBL. Larger organic initial concentrations lead to a longer lifetime of the coating but lead also to an unrealistically strong decrease of O_3 concentrations as the organic film is destroyed by reaction with O_3 . The lifetime of the film can be increased by either assuming smaller reactive uptake coefficients for O_3 or by assuming that a part of the organic surfactants react with OH. With regard to tropospheric chemistry we found that gas phase concentrations for chlorine and bromine species decreased due to the decreased mass transfer between gas phase and aerosol phase. Aqueous phase chlorine concentrations also decreased but aqueous phase bromine concentrations increased. Differences for gas phase concentrations are in general smaller than for liquid phase concentrations. Differences for gas phase NO_2 or NO are very small (less than 5%) whereas liquid phase NO_2 concentrations increased in some cases by nearly 100%.

1 Introduction

Aerosol particles are important constituents of the global climate system. With their ability to scatter solar radiation aerosols influence the global energy budget and affect

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climate directly. Furthermore, they serve as cloud condensation nuclei (CCN) and influence cloud properties like the number distributions and size of droplets. As the scattering of solar radiation depends on these quantities, aerosols also have an indirect effect on the global energy budget.

5 In the marine boundary layer sulfate and sea salt aerosols which originate from bubble bursting at the ocean surface are the most important particles which can act as CCN.

Apart from their role in cloud processes, aerosol particles are important for atmospheric chemistry as they can take up gas phase species, recycle them and release them back into the gas phase. Furthermore sea salt aerosol particles can be the source for gas phase constituents like halogen species.

More than 20 years ago Gill et al. (1983) investigated the potential importance of organic surfactants which can be present on sea salt aerosols and which might affect processes like droplet activation and droplet growth.

15 Recent measurements support this idea as they have shown that the organic mass fraction in marine particles can be up to 60% especially in regions with high biological activity (O'Dowd et al., 2004). Even in areas where only small amounts of microorganisms are present in sea water like the Caribbean (Novakov et al., 1997; Russell et al., 2002) and Cape Grim (Middlebrook et al., 1998) non-negligible organic mass fractions were detected. Organic concentrations in marine particle samples vary up to a few orders of magnitude since the biological activity varies and since the organic mass fraction is much larger in the smallest particle modes than in larger modes (O'Dowd et al., 2004). Cavalli et al. (2004) report concentrations of water insoluble organic compounds of $0.66 \mu\text{gm}^{-3}$ in the submicron and $0.26 \mu\text{gm}^{-3}$ in the supermicron mode whereas Sempere and Kawamura (2003) report dicarboxylic acid concentrations of only a few ngm^{-3} .

Both dissolved organic matter and decomposition products from algae accumulate in the surface microlayer. The thickness of this layer depends on the biological activity. Organic matter can be directly incorporated in marine particles when gas bubbles burst

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at the surface. Furthermore, rising gas bubbles scavenge organic material in the water column when they rise towards the surface. A third way for inclusion of organic matter into sea salt aerosol particles is uptake from the gas phase into airborne particles.

Although it is known that these processes take place it is still a challenge to determine the contribution from the oceanic surface microlayer to the initial chemical composition of sea salt particles which is important for understanding the complete reaction cycles taking place in the atmosphere.

As organic compounds are large in number and complexity most chemical analyses of sea salt aerosols can only give information about functional groups being present in the samples. The measurements from Mace Head have further shown that about 60% of the total organic mass fraction is water insoluble. The functional groups detected are mainly carbonyl compounds and carboxylic acids (Cavalli et al., 2004; Russell et al., 2002; Sempere and Kawamura, 2003; Mochida et al., 2002) which might be decomposition products of longer chain fatty acids. These compounds are known to be surface active meaning that they are able to form a film on the aerosol which can decrease the mass transfer between the gas phase and the liquid phase as discussed by Gill et al. (1983). However, laboratory measurements show different results regarding the degree of uptake reduction. While N_2O_5 uptake on sea salt aerosols covered by an organic coating seems to be decreased by a factor of about 10 (Thornton and Abbatt, 2005; Badger et al., 2000; Neill et al., 2006) there are measurements which show that uptake of water vapour on particles with a palmitic acid coating is not affected significantly (Garland et al., 2005).

Brown et al. (2006) have collected aerosol particles over the American continent and could show that the uptake coefficient for N_2O_5 on these particles varies with ambient conditions including the organic mass fraction in the aerosol supporting the results from the other laboratory measurements. It was assumed that organic surfactants might have a great influence on droplet activation and droplet growth. Ervens et al. (2005) presented a model study where they could show that the impact of organic surfactants on the microphysical properties of the aerosol might have been overestimated.

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Previously the effects caused by alteration of the aerosol's solubility, molecular weight and surface tension due to an organic coating counteract one another and lead to only small changes compared with cases where these effects are ignored.

As mentioned above little is known about the chemical composition of the organic mass fraction so that it is very difficult to assess the chemical reactions that take place on the organic aerosol surface and within the aerosol. What has been shown in many studies however, is that the surfactant coating undergoes chemical reaction with atmospheric oxidants like O_3 or OH which leads to the destruction of the organic coating on the aerosol. Most of the published laboratory studies dealing with the reactive uptake of O_3 on coated particles use oleic acid as a proxy for surface active compounds like fatty acids (Moise and Rudich, 2002; Smith et al., 2002; Katrib et al., 2004; Hearn and Smith, 2004; Thornberry and Abbatt, 2004; Knopf et al., 2005; Hung et al., 2005; Hearn et al., 2005; Ziemann, 2005; Zahardis et al., 2005; Katrib et al., 2005; Zahardis et al., 2006). Although the measurements agree quite well in the value for the reactive uptake coefficient it is questionable if these numbers can be applied under atmospheric conditions where an organic film would consist of a large number of different surfactants. One reason why we maybe should handle these data with care are the large discrepancies in oleic acid lifetimes in the laboratory where the molecules only survive a few seconds opposed to the lifetimes in the atmosphere which seem to be a few days. Robinson et al. (2006) calculated the oxidation lifetime of condensed phase organic aerosol constituents as a function of particle size and compared the results to the age of an aerosol particle in air masses which are affected by regional transport. They suggest that a reactive uptake coefficient for O_3 on organic aerosols nearly two orders of magnitude smaller than reported from laboratory measurements would be more realistic.

Apart from the uncertainties regarding the destruction rate of the film even less is known about reaction products that are formed by the reaction between the organic film with gas phase oxidants and further reaction pathways.

In this paper we investigate the influence of a decreased mass transfer between the

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gas phase and the liquid phase on atmospheric chemistry which we assume to be the dominant effect of a surfactant coating on sea salt aerosols for chemistry.

Based on model calculations we provide estimates about the lifetime of organic coatings in the atmosphere and up to which altitudes coated sea salt particles can be transported. The influence of the coating on gas phase and liquid phase chemistry is analysed with a special focus on halogen chemistry which is strongly influenced by gas and aerosol phase interactions and heterogeneous reactions.

In Sect. 2 of this paper a model description and the setup for the model runs is presented. In Sect. 3 the influence of a reduced mass transfer due to the organic coating on atmospheric gas and liquid phase chemistry is discussed.

2 Model description

For studying the effect of organic surfactants on atmospheric chemistry we use the one-dimensional numerical model MISTRA (von Glasow and Crutzen, 2004; von Glasow et al., 2002a,b) which is a model of the marine boundary layer (MBL). It contains a microphysics scheme and calculates chemistry in the gas phase, in aerosol particles and in cloud droplets. The chemical mechanism contains the most important reactions of O, H, C, N, S, Cl, and Br both in the gas and particulate phase and has been updated according to the IUPAC recommendation (04-2004, see <http://www.iupac-kinetic.ch.cam.ac.uk>).

In the model it can be distinguished between sulfate aerosols and sea salt aerosols which differ by their size ($r < 0.5 \mu\text{m}$ for sulfate, $r > 0.5 \mu\text{m}$ for sea salt) and initial chemical composition. The parameterisation of Monahan et al. (1986) for the emission of sea salt particles by bubble bursting is used.

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2.1 Surface reaction

As mentioned above we focus on limitations of mass transfer from gas to liquid and liquid to gas phase. The rate coefficients for heterogeneous reactions and phase transfer reactions depend on the mass transfer coefficient k_t for non-reactive uptake of gas molecules to the surface of particles (Schwartz, 1986) which is given by:

$$k_t = \left(\frac{r^2}{3D_g} + \frac{4r}{3\bar{v}\alpha} \right)^{-1} \quad (1)$$

with the particle radius r , the mean molecular speed $\bar{v} = \sqrt{8RT/(M\pi)}$ (M is the molar mass), the accommodation coefficient α and the gas phase diffusion coefficient D_g which can be approximated by $D_g = \lambda\bar{v}/3$ using the mean free path λ .

The parameter influenced by the organic coating is the accommodation coefficient which describes the probability that a gas phase molecule impinging on the particle is taken up.

To simulate organic surface films every sea salt particle which is emitted from the ocean is assumed to contain organic compounds. We assumed that one molecule of an organic compound covers $20 \times 10^{-20} \text{ m}^2$ of the sea salt aerosol surface. For a particle radius of $3 \mu\text{m}$ an organic concentration of about 0.5 nmol/l is needed to form a complete monolayer on the particle. In the following concentrations refer to the total sea salt particle spectrum so that the oleic acid mixing ratio to cover all sea salt particles would be about 0.07 mol/l for particles with an average radius of $3 \mu\text{m}$.

As soon as the organic concentration is large enough to form a monolayer on the aerosol the accommodation coefficients (α) for gas phase species are decreased in the model. A reduction of α by one order of magnitude would lead to a decrease in the transfer coefficient (k_t) of about 50% for a particle with a radius of $0.8 \mu\text{m}$. Figure (1) shows the effect for various reduction factors as a function of particle radius.

To describe the heterogeneous reaction between gas phase oxidants and the organic

surfactants the reactive uptake coefficient γ replaces the accommodation coefficient α in the mass transfer equation. That means that we use a reactive uptake coefficient instead of an unreactive uptake coefficient.

5 All model runs were performed for summer time (solar declination 20°) under clean marine conditions characterised by relatively low NO_x and O_3 mixing ratios. A typical marine background aerosol size distribution (Hoppel and Frick, 1990) with an initial surface area of $70 \mu\text{m}^2 \text{cm}^{-3}$ is used. We chose the initial and boundary conditions such that no clouds form during the simulation time and the boundary layer height is kept constant at about 700 m. The temperature in the lowest model levels is about
10 15°C and relative humidity increases from 65% near the ocean surface to 85% at the top of the boundary layer.

All model runs are initialised with the same fields for chemistry and meteorology which are taken from a two day model run without organic emissions in order to have a spin up for the model. The simulation time for all runs is three days and each run
15 starts at midnight. For all cases except the base case sea salt particles contain organic compounds when they are emitted from the ocean. This setup can be understood as follows: The model column moves over the clean ocean and after two days it crosses for three days an area with high biological activity where organic material gets incorporated into sea salt aerosols.

20 2.2 Halogen chemistry

The most important source for gas phase halogen species in the marine troposphere are sea salt aerosols. As soon as H^+ concentrations in the aerosol are large enough BrCl and Br_2 are formed in the aerosol and degas into the condensed phase starting a halogen cycling between the aerosol phase and the gas phase (Fig. 2) (Vogt et al.,
25 1996; von Glasow and Crutzen, 2003). Gas phase BrCl and Br_2 are rapidly photolysed during day and form Br and Cl . Both species can react with O_3 and produce the halogen oxides BrO and ClO which further react leading to the production of HOBr or HOCl . The two last named species are taken up by the aerosol where they take part

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in the acid catalysed reactions forming BrCl or Br_2 . BrO and ClO can further react with NO_2 and produce BrONO_2 and ClONO_2 which take part in heterogeneous reactions.

2.3 Setup of model runs

To quantify the uncertainties regarding the concentrations of organic compounds being present in sea salt aerosols, the magnitude of uptake reduction, the oxidation rate of the organics and the organic fractions being oxidised by reaction with ozone or OH four different scenarios were calculated. In the following we refer to the different scenarios with Roman numbers I–IV and to the different cases with Arabic numbers 1–6.

Scenario I: The first set of model runs for scenario I was performed to investigate the potential influence of different organic concentrations in sea salt aerosols. As mentioned above organic concentrations might vary by more than three orders of magnitude as they are strongly depending on ambient conditions.

For all cases of this scenario it is assumed that the surface film only comprises of oleic acid, which we use as a proxy for long chain organic surfactants and that the film is destroyed by reaction between oleic acid and O_3 using the literature values for the reactive uptake coefficient (Knopf et al., 2005). The accommodation coefficients of all species are decreased by a factor of 10 if an organic coating is present. The initial oleic acid concentrations are varied.

Scenario II: The uptake coefficients which we used for the heterogeneous reactions between the organic film compounds and gas phase radicals were all determined under laboratory conditions using single compound organic particles or particles covered by a single-compound-film. However, even a surface film consisting of only two different compounds changes the reactivity of the film (Katrib et al., 2005). In reality a surface film consists of a large number of different organic compounds. A mixed film might alter the chemical properties of a coated aerosol significantly in contrast to the laboratory studies. Therefore we performed model runs with different reaction rates for the reaction between oleic acid and O_3 . For this scenario the initial organic concentration was kept constant for all cases and all accommodation coefficients were reduced in the

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same way as in scenario I.

Scenario III: The uncertainty regarding the real composition of an organic film leads to the question how many surface molecules are really oxidised by reaction with O_3 and how many molecules react with other oxidants like OH. In scenario III the film consists of different mass fractions of oleic acid (which reacts with O_3) and “ORG” which is an unspecified organic compound which reacts with OH. The reactive uptake coefficient for this reaction is taken from [Bertram et al. \(2001\)](#). Again the accommodation coefficients are reduced by one order of magnitude if an organic film is present. Initial concentrations of both of the organic species were varied indicating that a film has different (ORG)/(oleic acid) ratios.

Scenario IV: Finally we studied the sensitivity of atmospheric gas and aerosol phase chemistry to different magnitudes of uptake reduction. In cases 1–3 of scenario IV the organic surface film consists again only of oleic acid which reacts with O_3 . The initial oleic acid concentration was the same for all three cases (same setup as case I.2). In cases 4–6 the film consists of oleic acid and ORG (same setup as case III.2). The decrease of the accommodation coefficients was varied.

3 Results

3.1 Lifetime of the organic film

Organic surface films on sea salt particles can only have an effect on atmospheric chemistry if they have a lifetime long enough so that they can be transported to higher levels of the MBL.

Scenario I: For case 1 of scenario I (blue dash dotted line, Fig. 3Ia, Ib, Ic) it was assumed that the initial oleic acid concentration for freshly emitted sea salt aerosols is large enough to form exactly one monolayer on the aerosol. The plots Ia, IIa and IIIa of Fig. 3 show the maximum altitude where particles with a complete monolayer can be found. As can be seen in Fig. 3Ia, for case I.1 the organic coating is already destroyed

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within the lowest 30 m of the boundary layer because the reaction with O_3 is very fast. For case I.2 (green dotted line, Figs. 3Ia, Ib, Ic) and case I.3 (red dashed line, Figs. 3Ia, Ib, Ic) higher initial organic concentrations were assumed. As a consequence, coated particles can be found at higher atmospheric levels during the whole simulation time (90 m for case I.2, 140 m (day) –200 m (night) for case I.3). The differences for case I.3 between day and night can be explained with the diurnal variation of the turbulence structure in the MBL. Turbulent transport is stronger during night than during day as the air cools down stronger at night than the ocean surface thus inducing thermal turbulence. That explains why coated particles can reach higher levels during night than during day when the sea salt source and the only sink reaction for organic surfactants stay unchanged.

However, the assumptions which were made in scenario I cannot be used for further investigations because after three days of model run we see a dramatic decrease in O_3 concentrations by 30% for case I.3 compared to the base run without an organic coating (Fig. 3Ic). For case I.1 and case I.2 where oleic acid concentrations are lower the differences are smaller. This effect is caused by the new sink reaction for O_3 with oleic acid. With a reactive uptake coefficient of $\gamma = 7.9 \times 10^{-4}$, the O_3 destruction rate by the heterogeneous reaction with oleic acid is 0.008 pmol/mol-s which results in the difference of 3.75 nmol/mol (for case I.3) after three days simulation time. Such a strong O_3 loss is not realistic.

Scenario II: Therefore, in scenario II the reactive uptake coefficients for O_3 on oleic acid are decreased. For case II.3 (red dashed line Fig. 3IIa, b) the same initial oleic acid concentration as in case I.1 (0.08 mol/l , blue dash dotted line Fig. 3IIa, b) which is the same as case II.1 (green dotted line Fig. 3IIa, b) is sufficiently large enough for the presence of coated particles at 500 m altitude during the whole simulation time, without an unrealistically strong O_3 destruction. By changing the reactivity of the film by about one order of magnitude (case II.2, blue dash dotted line, Fig. 3IIa) coated particles can be found up to about 100 m.

Scenario III: The lifetime of the film can also be increased when we assume that only

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a small fraction of the organic constituents react with O_3 and the largest fraction reacts with OH. For such a scenario an initial concentration of 0.062 mol/l for “ORG” and an oleic acid concentration of about 0.047 mol/l is sufficient to transport coated particles into upper levels of the boundary layer (case III.3, light blue line, Fig. 3IIIa). However, in case III.3 coated particles reach altitudes larger than 200 m only during day and the first hours of the nights. As explained above turbulent transport in the MBL is stronger during night than during day. For case I.3 for which we have chosen the largest initial concentrations for the organics this leads to a larger maximum altitude where coated particles can be found during night (200 m, see Fig. 3Ia).

For all cases of scenario III (and also cases II.2, II.3) it leads to the opposite effect because stronger turbulent transport also leads to a larger relative humidity during night in the upper levels of the MBL so that aerosol growth is facilitated leading to larger aerosol particles. That means that at altitudes of 200 m to 700 m the organic concentration which is needed to form a complete monolayer is slightly larger during night than during day. The concentration differences between cases III.1 (red dash dotted line, Fig. 3IIIa, b, c), III.2 (green dotted line, Fig. 3IIIa, b, c), III.3 (light blue line, Fig. 3IIIa, b, c) and III.4 (black line, Fig. 3IIIa, b, c) at these altitudes are very small but sufficiently large to find coated particles at 500 m altitude also during night in case III.1 and III.2 but not in case III.3. and III.4

In case III.5 (blue dashed line, Fig. 3IIIa, b, c) and case III.6 (purple line, Fig. 3IIIa, b, c) where oleic acid and “ORG” concentrations were low but the reactivity of the film was decreased, coated particles can reach at least an altitude of about 100 m to 300 m.

In an additional model run which is not included in Table 1 the organic film comprises of 50% oleic acid (0.04 mol/l) and 50% “ORG” (0.04 mol/l) and the total organic concentration in the lowest model level is as large as needed to form exactly one monolayer (0.08 mol/l) on the sea salt aerosol and the literature values for the reactive uptake coefficients are used. The film is again already destroyed within in the first 30 m of the MBL which is the same effect as observed for case I.1.

Even though the reactive uptake coefficient for OH on organic aerosols is much

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larger than the reactive uptake coefficient for O_3 on oleic acid the reaction velocity for the reaction $OH + ORG$ is not as fast as for $O_3 + \text{oleic acid}$. OH is a very short lived radical with concentrations that are several orders of magnitude lower than for O_3 which has a much longer lifetime. Furthermore, gas phase sink reactions for OH are up to three orders of magnitude faster than the heterogeneous reaction with the organic film. In contrast to this the reaction with the surfactants becomes one of the fastest O_3 sink reactions leading to its strong destruction as discussed above. This explains the slow destruction of the organic film if it predominantly reacts with OH . For scenario III the lifetime of the film is further increased because OH is not present during night and no other sink reaction for the organic surfactants (“ORG”) are taken into account.

The different cases show that vertical transport mainly controls the magnitude of the influence of surfactants on atmospheric chemistry. Variations of the initial concentration in the range of mmol/l lead to significant differences in the maximum altitude where surfactants can still form a monolayer. However, it is not possible to determine a threshold for the initial organic surfactant concentration below which their influence is negligible. We made the assumption that one molecule oleic acid is located directly next to the adjacent molecule but it might be possible that organics do not have to be packed this tightly on the aerosol surface to influence mass exchange between gas and liquid phase. Laboratory measurements show that a monolayer of loosely packed organic compounds can still have an influence on the uptake behaviour (Neill et al., 2006) so that we might overestimate initial surfactant concentrations in our model. Furthermore, decomposition products of the initial organic compounds might still be surface active increasing the effect of a decreased mass transfer.

One can conclude that:

- If 50% of the organics were to react with OH and 50% with O_3 and reactive uptake coefficients determined in the laboratory are valid under atmospheric conditions, then the initial concentration of both species have to be larger than 0.04 mol/l so that coated particles are present in the lowest 50 m of the MBL or above.

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- If more than 50% of the organics react with OH, an initial ORG concentration of 0.07 mol/l and an initial oleic acid concentration of 0.078 mol/l is enough to find covered particles even at 400–500 m altitude (case III.2).
- To survive long enough in the atmosphere to be important, either i) the largest fractions of the organic film have to be compounds that react with OH (or at least that do not react with O₃) when assuming that measured reactive uptake coefficients are correct (cases III.2, III.3), or ii) if about 50% of the organics should react with O₃ (cases II.2, III.6) the reaction rates have to be about a factor of five smaller than those from the laboratory.

3.2 Effects of reduced mass transfer on chemistry

The net effect of the decreased mass transfer due to an organic coating on atmospheric chemistry mainly depends on the lifetime of the film. Therefore results from scenario II and III are very similar and only scenario III is discussed in more detail in this section. It can be expected that especially those species are mostly influenced by the decreased mass transfer due to an organic coating that i) directly take part in heterogeneous reactions or uptake processes; or ii) species that take part in acid catalysed reactions.

Sea salt aerosols get rapidly acidified in the atmosphere by uptake of acids like HNO₃ or H₂SO₄. These processes are slowed down by the organic surface film leading to slightly higher gas phase concentrations and lower aqueous phase concentrations of acids in contrast to the base case. Although the uptake of acids is decreased, the decrease of H⁺ concentrations is relatively small and the aerosol pH is hardly changed when it is compared with the base case (Fig. 5). Only in the case with highest rates for the surface reaction (case III.1) the pH increases from 5.60 to 5.65 at day three of the simulation time. These differences are too small to influence aqueous phase chemistry and acid catalysed reactions significantly.

We focus our discussion on tropospheric halogen chemistry because concentrations of halogen species are strongly controlled by exchange processes between the gas

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and the aqueous phase as well as by the acidity of the aerosol.

In Fig. 4 the mixing ratios of total gas phase bromine and chlorine species are plotted. For all cases the concentrations are lower than without an organic coating (black line) which has to be attributed to the decreased mass transfer out of the liquid phase.

However, the difference after three days of simulation time is only 9% for total bromine. For gas phase chlorine concentrations the same effect can be observed but the differences are larger (10%–20% for case III.1). This trend can be observed for nearly all species, i.e. ΔCl : 20–30%, ΔClO : 20–40%, ΔCl_2 : 50–80%, ΔHOCl : 10–30% versus ΔBr : 5–15%, ΔBrO : 15–25%, ΔBr_2 : 20–30% or ΔHOBr : 15–20%.

During day, one of the main sources for gas phase Cl and Br is photolysis of BrCl which degasses out of the aerosol. Due to the organic coating less BrCl gets into the gas phase leading to a reduced Cl and Br production by this reaction pathway (Fig. 2). A second important source for Br is the photolysis of Br_2 which also degasses more slowly out of the aerosol when an organic coating is present. A respective source for Cl is photolysis of Cl_2 . However, this reaction is about 80% slower than photolysis of Br_2 . The lower Br and Cl gas phase concentrations lead to lower concentrations of their reaction products like HOBr, HBr, BrONO_2 and, respectively, HOCl, HCl and ClONO_2 which are taken up by the aerosol or take part in heterogeneous surface reactions (ClONO_2 , BrONO_2). Uptake and surface reactions are also slowed down so that less bromine and chlorine get into the aerosol phase compared to the base case.

In Fig. 5 concentrations of aqueous phase HOBr and HOCl are plotted. It can be seen that HOCl concentrations decreased and HOBr concentrations increased when an organic coating was present on sea salt aerosols compared to the base case. A very important reaction for starting bromine chemistry in the aqueous phase is the conversion of Br^- into Br_2 or BrCl by the following reactions:



Both reactions are equilibrium reactions which usually produce Br_2 and BrCl in the for-

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ward Reactions (2, 3). If the organic film is present Br_2 and BrCl accumulate in the aqueous phase because the transfer into the gas phase is decreased. As a consequence the reverse Reactions (−2,−3) gain in importance and produce HOBr and Br^- leading to larger HOBr aqueous phase concentrations compared to the base case.

- 5 Equivalent reactions take place including HOCl instead of HOBr and lead to the production of Cl_2 and BrCl without considering the effect of the organic coating.



- 10 However, these reactions are slower and the reverse reaction of Reaction (5) is negligible. As a result with an organic coating more HOCl is consumed because of larger Br^- concentrations but less Cl_2 is produced because Cl^- concentrations are hardly affected by the coating.

- 15 The shifting of the equilibria due to the decreased mass transfer between gas phase and liquid phase explains the increased concentrations of aqueous phase bromine species. For aqueous phase chlorine this shift does not take place which explains the decreased concentrations in comparison with the base case. Fig. 5 also shows the bromine enrichment factor which is defined as follows:

$$EF(\text{Br}) = \frac{\left(\frac{[\text{Br}^-]}{[\text{Na}^+]} \right)_{\text{particle}}}{\left(\frac{[\text{Br}^-]}{[\text{Na}^+]} \right)_{\text{seawater}}} \quad (6)$$

- 20 The Br enrichment factor is about 30–40% higher for case III.1 compared to the base run. This case shows the largest differences because the lifetime of the organic coating is longer than in other cases and sea salt aerosols which contain a surfactant monolayer reach larger altitudes than in the other simulated cases. Other bromine species like HOBr , BrCl , HBr show differences in the range of 30% compared to the base case

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(in contrast to about 20% in the gas phase). HOCl aqueous phase concentrations decrease by about 40–50%. Aqueous phase chemistry seems to be affected more by organic coatings than gas phase chemistry.

As less aqueous phase chlorine is present in model runs with a surfactant coating even less chlorine can degas in comparison to bromine and in comparison with the base case. This explains why gas phase chlorine concentrations decrease much stronger than bromine concentrations. When less gas phase chlorine is produced, smaller amounts can also be taken up by the aerosol so that the effect intensifies itself. Apart from halogen chemistry other species are also affected by the decreased mass transfer due to the organic film. For the aqueous phase higher concentrations for NO_2 (ΔNO_2 : 100%), NO_2^- , HONO and NO_3 can be observed as the concentrations of these species depend on uptake processes. However, the absolute concentrations of all those species are very low so that the relatively small deviation from the base case do not influence any other processes.

For the gas phase nearly no difference in NO , NO_2 or N_2O_5 concentrations are found. However, all model runs were performed under clean marine conditions with very low NO_x mixing ratios.

3.2.1 Impact of magnitude of uptake decrease

In all scenarios discussed above it was assumed that if sea salt aerosols are completely covered with an organic monolayer the accommodation coefficient is reduced by one order of magnitude. Literature values for the strength of uptake reduction vary from a factor of 3–4 (Thornton and Abbatt, 2005) to a factor of 42 (Badger et al., 2000). To quantify how chemistry responds to different uptake behaviour onto sea salt aerosols we performed sensitivity studies where the accommodation coefficients for gas phase species were reduced by various orders of magnitude (Table 1, scenario IV). For cases IV.1–IV.3 the initial organic concentrations were relatively low so that the maximum altitude where particles with a complete monolayer can be found is 90 m (similar setup than for case I.2, Fig. 3Ia, green line). For cases IV.4–IV.6 the same

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initial conditions were chosen as for case III.2 so that coated particles can be found at 400 m altitude during the whole simulation time (Fig. 3IIIa, green dotted).

In Fig. 6 time series of total gas phase chlorine and total gas phase bromine concentrations at 70 m altitude are plotted for scenario IV. Apparently gas phase chemistry is not very sensitive to the magnitude of uptake reduction for cases IV.1–IV.3 (Fig. 6a–d). A decrease of the accommodation coefficient by a factor of 4 (case IV.1) leads to 4% smaller concentrations for total Br and about 6% smaller concentrations for total Cl compared to the base case. Surprisingly, the concentrations hardly decrease any further (6% for Br and Cl) in case IV.3 where uptake was decreased by about two orders of magnitude. Similar effects can be observed for nearly all gas phase species. As a decrease of the accommodation coefficient by two orders of magnitude leads to a decrease of the mass transfer coefficient by about one order of magnitude (Fig. 1) the differences in reaction velocities for the cases of scenario IV are less than an order of magnitude.

Larger differences between the three cases can be observed for the liquid phase like it can be expected from the results from scenario III. The Br enrichment factor is increased by 10–30% for case IV.1, 20–40% for case IV.2 and 40–90% for case IV.3 compared to the base case. The differences increase with simulation time indicating that the enrichment of Br in the aerosol due to the organic coating gets stronger the longer the monolayer is present.

Sea salt pH does not increase significantly for cases IV.1 and IV.2 but it increases from about 5.6 (base case, day 3) to about 6 for case IV.3. In comparison with the results from scenario III a long-lived organic coating with a relatively low uptake reduction (scenario III) has more influence on atmospheric chemistry than a short-lived organic monolayer with a relatively large uptake reduction (scenario IV, case 1–3).

For cases IV.4–IV.6 where the lifetime of the organic coating is long, chemistry is much more sensitive to the magnitude of uptake reduction as can be seen in Figs. 6e and f. When the destruction of the organic coating is slow and the accommodation coefficient is reduced by about two orders of magnitude total bromine concentrations

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decrease by about 20% and the enrichment factor increases even by about 100%.

4 Conclusions

With our model simulations we could show that if the majority of the organic surfactants react with ozone and we use the measured reactive uptake coefficient for ozone on oleic acid we get a dramatic decrease in ozone concentrations after three days of simulation time. This clearly shows that either:

1. Oleic acid is not a representative substance for atmospheric long chain fatty acids.
2. The real composition of the surfactant coating which contains a lot of different organic compounds alters the uptake behaviour in such a way that the reactive uptake coefficients from laboratory studies cannot be applied under atmospheric conditions.
3. Only a very small fraction of the organic surfactants react with O_3 and the largest fraction reacts with OH or with other oxidants like NO_3 .

We investigated the influence of a reduced mass transfer between gas phase and aerosol phase caused by an organic surfactant coating on tropospheric chemistry with special focus on halogen species. Our simulations show that gas phase bromine and chlorine concentrations decrease in the presence of an organic monolayer on sea salt aerosols. Chlorine gas phase chemistry is affected stronger than bromine chemistry. For the aqueous phase we observed an increase in bromine concentrations and a decrease in chlorine concentrations.

Gas phase chemistry apart from halogen chemistry is hardly influenced by the decreased mass transfer. Differences for example in NO_2 or NO concentrations are less than 5% whereas aqueous phase concentrations for NO_2 increase by nearly 100%.

Even though the presence of a coating reduces the uptake of acids, sea salt pH is not influenced until we decrease uptake by nearly two orders of magnitude.

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We have shown that under conditions where the lifetime of the organic coating is large enough so that coated particles can be found in upper levels of the boundary layer during the whole simulation time tropospheric chemistry might be affected by the decreased mass transfer due to the organic coating. However, very small changes in the model setup lead to large differences in the behaviour of the surfactants pointing out the existing uncertainties. For further investigating the influence of organic surfactants on atmospheric chemistry it is necessary to get more and detailed data about organic compounds which are found in the marine boundary layer and about a more realistic composition of the organic coating and its properties. Reactive uptake coefficients for mixed coatings are needed as well as information about decomposition products of long chain organic compounds and their reactivity.

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Table 1. α_o : accommodation coefficient, α : decreased accommodation coefficient, OA: initial concentration of oleic acid (respectively ORG) which sea salt particles contain when they are emitted from the ocean, $\gamma_{(OA)}$: reactive uptake coefficient for O_3 on oleic acid, $\gamma_{(org)}$: reactive uptake coefficient for OH on “ORG”.

Scenario I		Scenario II	
$\alpha = 0.1 \cdot \alpha_o$ $\gamma_{(OA)} = 7.9 \times 10^{-4}$	case 1: OA=0.08 mol/l	OA=0.08 mol/l	case 1: $\gamma_{(OA)} = 7.9 \times 10^{-4}$
	case 2: OA=0.4 mol/l	$\alpha = 0.1 \cdot \alpha_o$	case 2: $\gamma_{(OA)} = 1 \times 10^{-5}$
	case 3: OA=0.8 mol/l		case 3: $\gamma_{(OA)} = 1 \times 10^{-6}$
Scenario III		Scenario IV	
$\alpha = 0.1 \cdot \alpha_o$ $\gamma_{(OA)} = 7.9 \times 10^{-4}$ $\gamma_{(Org)} = 0.1$	case 1: OA=0.39 mol/l Org=0.39 mol/l	OA=0.4 mol/l $\gamma_{(OA)} = 7.9 \times 10^{-4}$	case 1: $\alpha = 0.25 \cdot \alpha_o$
	case 2: OA=0.07 mol/l Org=0.078 mol/l		case 2: $\alpha = 0.1 \cdot \alpha_o$
	case 3: OA=0.047 mol/l Org=0.062 mol/l		case 3: $\alpha = 0.025 \cdot \alpha_o$
$\gamma_{(OA)} = 1 \times 10^{-5}$	case 4: OA=0.039 mol/l Org=0.055 mol/l	OA=0.07 mol/l Org=0.078 mol/l	case 4: $\alpha = 0.25 \cdot \alpha_o$
	case 5: OA=0.039 mol/l Org=0.047 mol/l	$\gamma_{(Org)} = 0.1$	case 5: $\alpha = 0.1 \cdot \alpha_o$
	case 6: OA=0.039 mol/l Org=0.039 mol/l		case 6: $\alpha = 0.025 \cdot \alpha_o$

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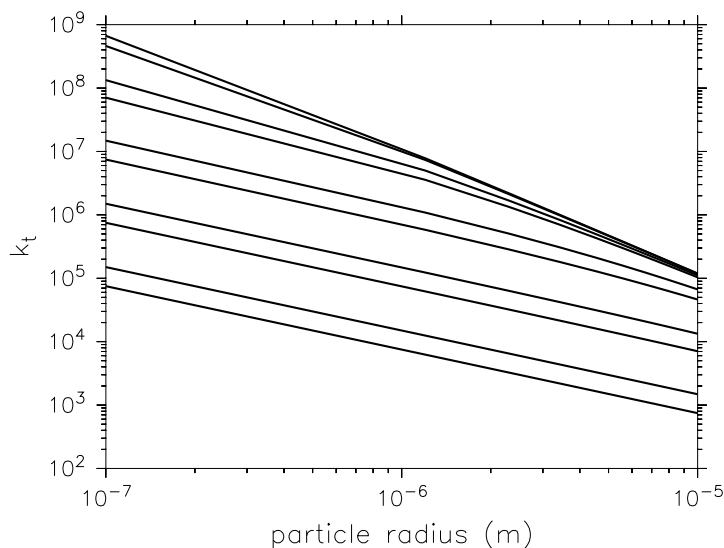
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Fig. 1. Transfer coefficient k_t as a function of particle radius and accommodation coefficient α calculated after Eq. (1). The largest value chosen for α was 1 (resulting in the largest values for k_t ; $k_t = 7 \times 10^8$ for $r = 10^{-7}$) and the lowest value was $\alpha = 5 \times 10^{-5}$ (resulting in the lowest value for k_t ; $k_t = 7 \times 10^4$ for $r = 10^{-7}$). α was decreased stepwise by a factor of 0.5 from 1 to 5×10^{-5} . The different lines refer to the transfer coefficient calculated with different accommodation coefficients. Note the logarithmic scaling of the axes.

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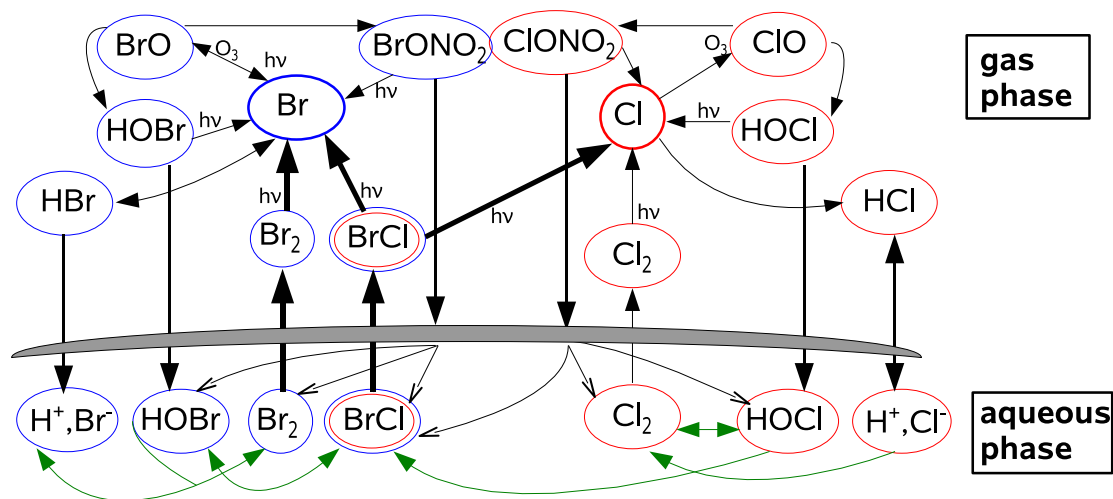


Fig. 2. Bromine and Chlorine cycling between aerosol phase and gas phase.

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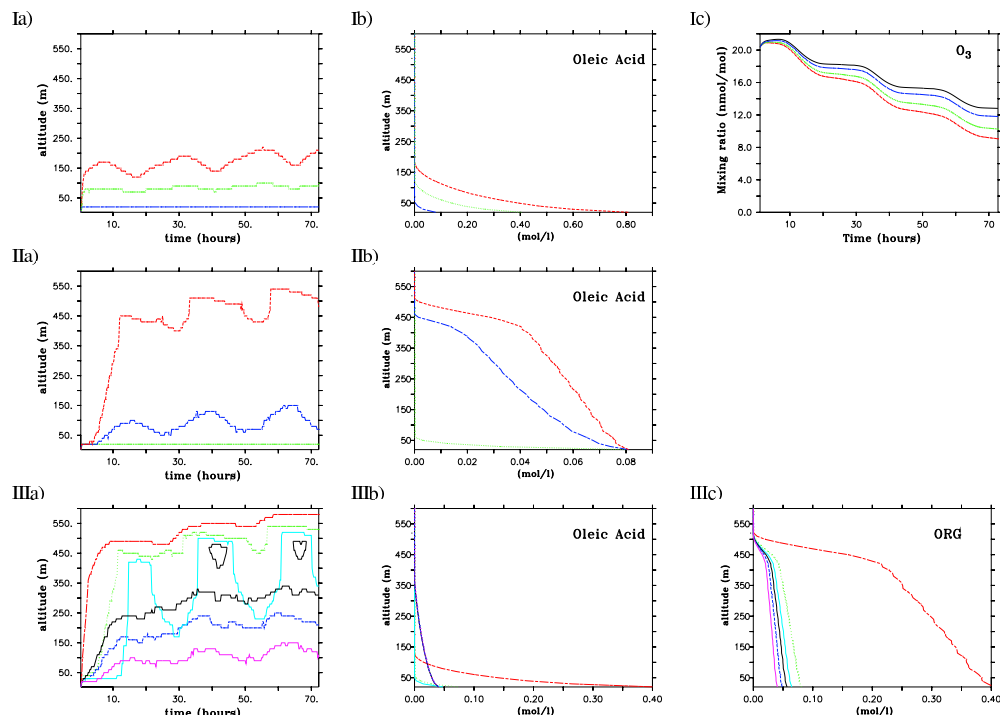
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Fig. 3. The colour code for the plots is as follows: plots for cases of Scenario I (Ia, Ib, Ic): base case (black solid), I.1 (blue dash-dotted), I.2 (green dotted), I.3 (red dashed). Plots for cases of Scenario II (IIa, IIb): II.1 (green), II.2 (blue), II.3 (red). Plots for cases of Scenario III (IIIa, IIIb, IIIc): III.1 (red), III.2 (green), III.3 (light blue), III.4 (black), III.5 (blue), III.6 (purple).

Figures Ia, IIa, IIIa: Levels below which sea salt aerosols are coated with an organic film. Figures Ib, IIb, IIIb: Vertical profile of oleic acid concentrations at noon, third day of simulation. As for scenario III, case III.4, III.5 and III.6 initial oleic acid concentrations were the same, the lines for these cases lie over each other (IIIb). Figure Ic: 3-days time series of gas phase O_3 mixing ratios at 50 m altitude. Figure IIIc: Vertical profile of “ORG” concentrations at noon, third day of simulation.

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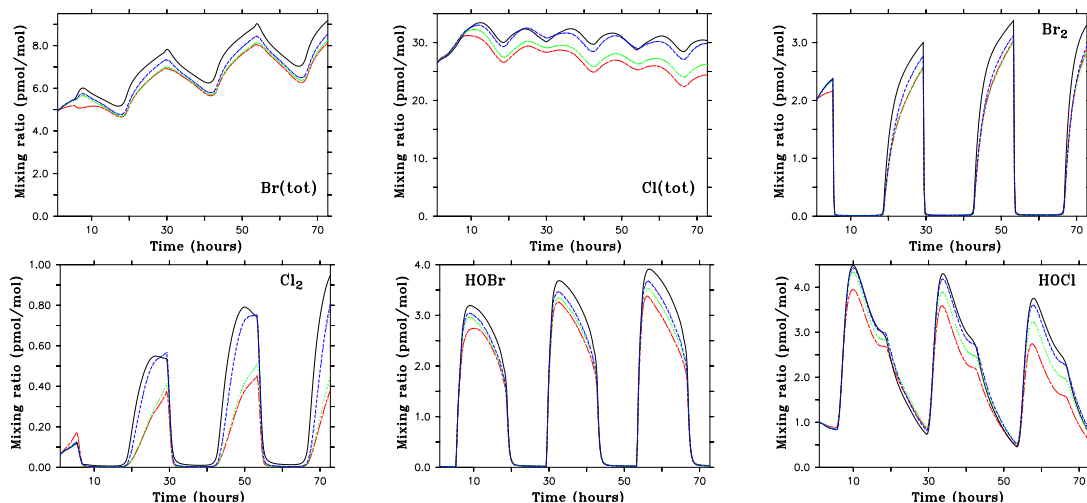
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Fig. 4. Scenario III: Time evolution of gas phase mixing ratios at 50m altitude for three days (midnight day 1 – midnight day 3). Case III.1 (red, dash dotted), case III.2 (green, dotted), case III.5 (blue, dashed), base case (black, solid line).

$$\text{Br}_{\text{tot}} = \text{HBr} + \text{HOBr} + \text{BrNO}_2 + \text{BrNO}_3 + 2 \cdot \text{Br}_2 + \text{BrCl} + \text{Br} + \text{BrO}$$

$$\text{Cl}_{\text{tot}} = \text{HCl} + \text{HOCl} + \text{ClNO}_2 + \text{ClNO}_3 + 2 \cdot \text{Cl}_2 + \text{Cl} + \text{ClO} + \text{OCIO} + 2 \cdot \text{Cl}_2\text{O}_2 + \text{BrCl}$$

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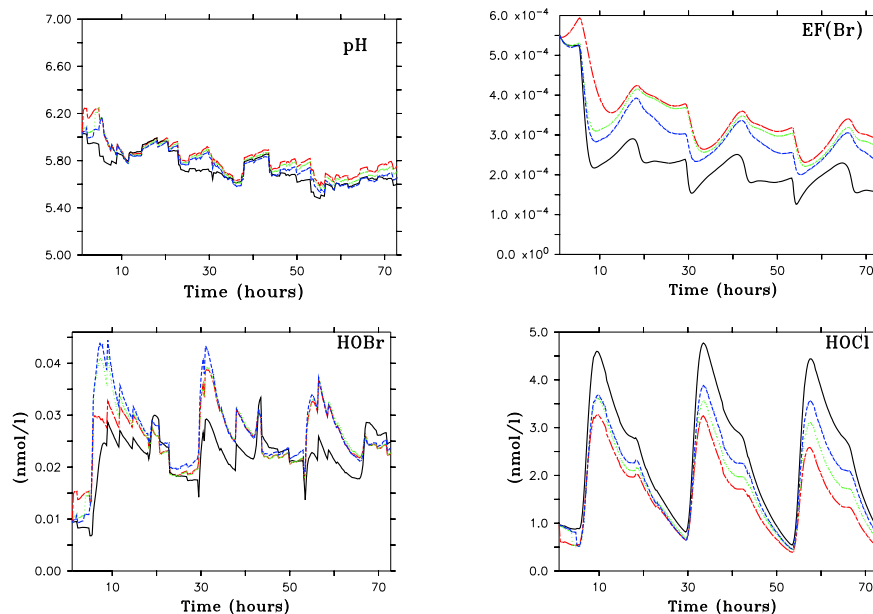
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Fig. 5. Scenario III: Time evolution of aqueous phase concentrations at 50 m altitude for three days (midnight day 1 – midnight day 3). Case III.1 (red, dash dotted), case III.2 (green, dotted), case III.5 (blue, dashed), base case (black, solid line).

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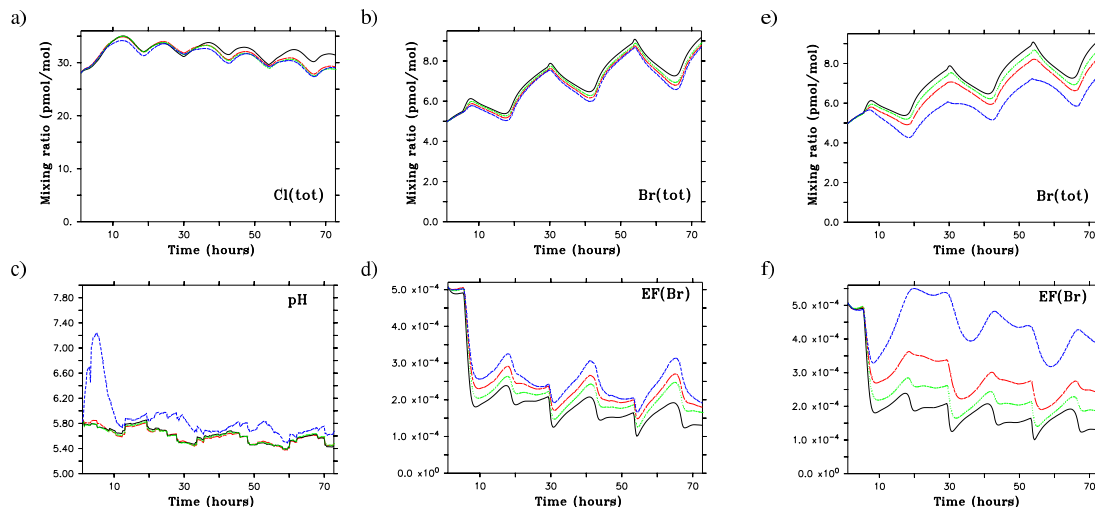
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Fig. 6. Scenario IV: Upper row: Mixing ratios of total gas phase bromine and chlorine. Lower row: Bromine enrichment factor and pH. All plots show time series at 70 m altitude for three days (midnight day 1 – midnight day 3).

Plots a)–d) refer to cases IV.1–IV.3. The colour code is as follows: case IV.1 (green, dotted), case IV.2 (red, dash dotted), case IV.3 (blue, dashed), base case (black, solid line). Plots e), f) refer to cases IV.4–IV.6. The colour code is as follows: case IV.4 (green, dotted), case IV.5 (red, dash dotted), case IV.6 (blue, dashed), base case (black, solid line).

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